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Fluorous Polymeric Membranes for Ionophore-Based Ion-Selective Potentiometry: How Inert Is Teflon AF?

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Abstract: Fluorous media are the least polar and polarizable condensed phases known. Their use as membrane materials considerably increases the selectivity and robustness of ion-selective electrodes (ISEs). In this research, a fluorous amorphous perfluoropolymer was used for the first time as a matrix for an ISE membrane. Electrodes for pH measurements with membranes composed of poly[4,5-difluoro-2,2-bis(trifluoromethyl)-1,3-dioxole]-*co*-poly(tetrafluoroethylene) (87% dioxole monomer content; known as Teflon AF2400) as polymer matrix, a linear perfluorooligoether as plasticizer, sodium tetrakis[3,5-bis(perfluorohexyl)phenyl]borate providing for ionic sites, and bis[(perfluorooctyl)propyl]-2,2,2-trifluoroethylamine as H^+ ionophore were investigated. All electrodes had excellent potentiometric selectivities, showed Nernstian responses to H^+ over a wide pH range, exhibited enhanced mechanical stability, and maintained their selectivity over at least 4 weeks. For membranes of low ionophore concentration, the polymer affected the sensor selectivity noticeably at polymer concentrations exceeding 15%. Also, the membrane resistance increased quite strongly at high polymer concentrations, which cannot be explained by the Mackie−Meares obstruction model. The selectivities and resistances depend on the polymer concentration because of a functional group associated with Teflon AF2400, with a concentration of one functional group per 854 monomer units of the polymer. In the fluorous environment of these membranes, this functional group binds to Na^+, K^+, Ca^{2+}, and the unprotonated ionophore with binding constants of $10^{3.5}$, $10^{1.8}$, $10^{6.8}$, and $10^{4.4}$ M^{-1}, respectively. Potentiometric and spectroscopic evidence indicates that these functional groups are COOH groups formed by the hydrolysis of carboxylic acid fluoride (COF) groups originally present in Teflon AF2400. The use of higher ionophore concentrations removes the undesirable effect of these COOH groups almost completely. Alternatively, the C(=O)F groups can be eliminated chemically, or they can be used to readily introduce new functionalities.

Introduction

Ionophore-doped ion-selective electrodes (ISEs) with wide ranges of linear responses, high selectivities, and low detection limits have become a routine tool in chemical analysis.[1−4] The ion-selective membranes of these sensors typically consist of an ionophore-doped and plasticized polymer, which provides for mechanical stability and elasticity.[5] The polarity and coordinating properties of the polymer and plasticizer have a large impact on the sensing performance.[3,4,6] A weakly coordinating matrix favors stronger binding of the ion receptor (ionophore) to the ions for which the sensor is designed, and weak solvation of interfering ions further increases the selectivity. Moreover, weak solvation of counterions inhibits their coextraction into ISE membranes (Donnan failure) and thereby widens the response range of these sensors.[6−10] We wish to take the benefits of noncoordinating and poorly solvating membrane matrixes to the ultimate limit by using the least polar, least polarizable phases known, that is, fluorous phases.[11−14] The very low polarity of fluorocarbons is illustrated, for example, by the π^* scale of solvent polarity, on which cyclohexane defines 0, water has a π^* value of 1.09, and

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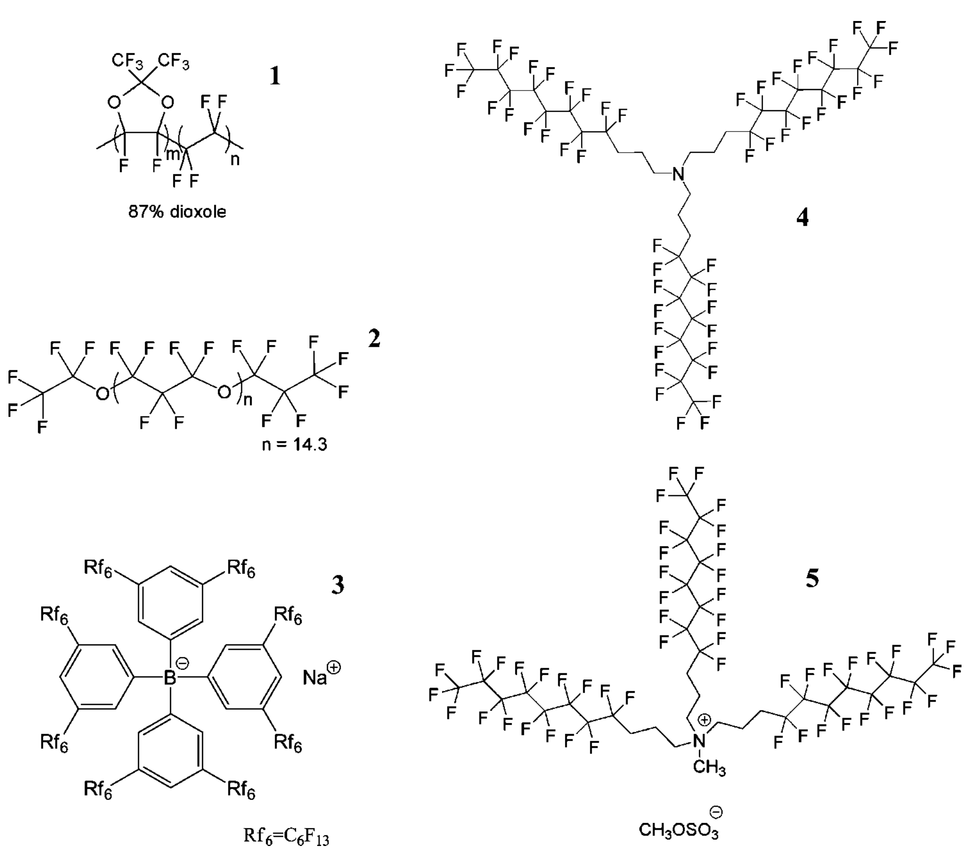
Chart 1



perfluorooctane has the astounding value of −0.41.[15,16] The extremely low polarity of fluorous phases arises from local symmetry as well as the very low polarizability of C−F bonds. Indeed, the very low solubility of lipids in fluorous phases is a significant advantage in view of reduced biofouling of ISE membranes.[13,17]

For our initial work with fluorous phases, we used perfluoroperhydrophenanthrene as matrix, and we developed several fluorophilic salts as ion exchanger sites and electrolyte salts. The first cation exchanger-based ISE with a fluorous membrane was shown to exhibit a selectivity range 8 orders of magnitude wider than for conventional sensors,[7,8] and an anion sensor gave the selectivity of 3.9×10^{10} to 1 for perfluorooctanesulfonate over Cl^-.[18] Also, a series of fluorophilic ionophores for H^+ have been used recently for the first ionophore-based ISEs with fluorous sensing membranes.[19] However, the perfluoroperhydrophenanthrene-based matrix of this first generation of fluorous membrane ISEs had only a limited mechanical stability. For routine measurements, there is a need to develop mechanically more robust polymeric fluorous sensing membranes. Unfortunately, only few currently available perfluoropolymers are suitable for the preparation of ISE membranes. To ensure that the electrical resistance of ISE membranes is not too high to prevent practical use, at least one ionic species must be able to move freely through these membranes. This requires that the glass transition temperature, T_g, of the sensing membrane is lower than the temperature at which measurements are performed;[20] changes in diffusion coefficients by as much as 6 orders of magnitude have been reported near the T_g.[21] Therefore, many crystalline or semicrystalline perfluoropolymers, such as the well-known poly(tetrafluoroethylene), are not suitable for use as a matrix for the ionophore-doped sensing membranes of ISEs. While a promising report in the literature discussed the plasticization of poly[4,5-difluoro-2,2,-bis(trifluoromethyl)-1,3-dioxole]-*co*-poly(tetrafluoroethylene) with a highly fluorinated plasticizer,[22] the latter contained a terminal carboxylic acid group, which can strongly interact with various ions and would reduce the potentiometric selectivity of ionophore-doped membranes.

With a view to applications in chemical sensing, we have, therefore, previously studied the plasticization of amorphous poly[4,5-difluoro-2,2,-bis(trifluoromethyl)-1,3-dioxole]-*co*-poly(tetrafluoroethylene) copolymers with dioxole monomer contents of 65% (Teflon AF1600) or 87% (Teflon AF2400, **1**, Chart 1), respectively, using plasticizers without polar functional groups.[23] A linear perfluorooligoether (**2**) with an average of 14.3 ether groups per molecule was the most successful plasticizer, as its blends with Teflon AF2400 or Teflon AF1600 provided T_g values as low as −114 °C. In the present work, ionophore-based ISEs with fluorous polymeric matrixes are reported. It is

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shown how the concentration of Teflon AF2400 in the blends with the linear perfluorooligoether affects the electrical resistance, response slope, selectivities, and long-term stability of ISEs with fluorous membranes. A detailed data analysis not only confirms that the ions Na^+, K^+, and Ca^{2+} interact only very weakly with the dioxole units of Teflon AF2400, but also reveals that Teflon AF2400 contains a functional group of very low concentration that interacts quite strongly with the ionophore and Ca^{2+}. Potentiometric and spectroscopic evidence to identify the character of these functional groups is presented. By describing the cation-binding properties of the ideal Teflon AF backbone and revealing the presence of C(=O)F groups in this polymer, this Article describes not only a sensor application but also addresses the more fundamental question of the inertness of Teflon AF, which has been widely used in physics, optics, electronics, electrochemistry, and analytical, polymer, surface, materials, and environmental chemistry.

Experimental Section

Reagents. All chemicals were of the highest commercially available purity and were used as received, unless noted otherwise. Teflon AF2400 (poly[4,5-difluoro-2,2-bis(trifluoromethyl)-1,3-dioxole-*co*-tetrafluoroethylene] with 87% dioxole monomer content, $T_g = 240$ °C), **1**, and Krytox157FS-H (α-(heptafluoropropyl)-*ω*-[1-(1-carboxy-1,2,2,2-tetrafluoroethyl)]-poly[oxy(1,1,1,2,3,3-hexafluoro-2,3-propanediyl)], MW = 7000−7500) were purchased from Sigma-Aldrich (St. Louis, MO), the linear perfluorooligoether α-(heptafluoropropyl)-*ω*-(pentafluoroethoxy)-poly[oxy(1,1,2,2,3,3-hexafluoro-1,3-propanediyl)] (MW = 2700, $T_g = -116$ °C), **2**, from Alfa Aesar (Ward Hill, MA), perfluorohexane from Synquest Laboratories (Alachua, FL), and 1-propylamine from Lancaster Synthesis (Pelham, NH). Sodium tetrakis[3,5-bis(perfluorohexyl)phenyl]borate (**3**), tris[(perfluorooctyl)propyl]amine (**4**), and tris[(perfluorooctyl)propyl]methylammonium methyl sulfate (**5**) were prepared according to previously described procedures.[7,8,24,25] Deionized and charcoal-treated water (18.2 MΩ cm specific resistance) obtained with a Milli-Q PLUS reagent-grade water system (Millipore, Bedford, MA) was used for all sample solutions. Tris(hydroxymethyl)aminomethane (99.8+%) and hydrochloric acid (1.0 M) were purchased from Sigma-Aldrich. All reference pH buffer solutions were purchased from VWR International (West Chester, PA) or Sigma-Aldrich.

Sensing Membranes. Fluoropore membrane filters (pure poly(tetrafluoroethylene) without backing, 47 mm diameter, 0.45 μm pore size, 50 μm thick, 85% porosity) were obtained from Millipore. The Fluoropore membrane filters were sandwiched between two note cards and cut with a hole punch to give small disks of 13 mm diameter. One layer of these filter disks was used for each membrane matrix.

Ionophore-doped sensing membranes were prepared from linear perfluorooligoether, Teflon AF2400, 0.5 mM sodium tetrakis[3,5-bis(perfluorohexyl)phenyl]borate, and 2 mM tris[(perfluorooctyl)propyl]amine. To prepare the membranes, ionic sites were first added into plasticizer and gently heated with a heat gun to completely dissolve the salt. Ionophore and (if applicable) perfluoropolymer were added into the solution after it had cooled back to room temperature. The whole mixture was then dissolved in perfluorohexane and stirred for at least 24 h. Upon application of the fluorous solution (20−60 μL, depending on the amount of perfluorohexane) with a micropipette to the surface of the porous filter disks and spontaneous evaporation of the perfluorohexane, the latter appeared translucent. The minimum content of Teflon AF2400 that gave mechanically stable membranes without a porous inert support was 30% (wt/wt).

For membranes used in ionophore-free ion exchanger electrodes, a saturated solution of sodium tetrakis[3,5-bis(perfluorohexyl)phenyl]borate in linear perfluorooligoether was prepared in the same way. Excess salt was removed by filtering through glass wool 1 day after the preparation of the suspension, and the Teflon AF2400 (30%, wt/wt) was then added. The mixture was dissolved in perfluorohexane (approximately 2 mL per 200 mg of membrane components) by stirring for 24 h. Finally, the solution was poured into a custom-machined Teflon dish (25 mm i.d.) to let the perfluorohexane evaporate slowly over 6 days. The thickness of the resulting membranes was 0.13 ± 0.01 mm.

Electrodes. The thus-prepared polymeric fluorous membranes were mounted into custom-machined electrode bodies made from poly(chlorotrifluoroethylene). A screw cap with a hole (8.3 mm diameter) in the center was screwed onto the electrode body, securing the membrane between the electrode body and the cap but leaving the center of the membrane exposed (see Figure 1 in ref 8). Inner filling solution (10 mM LiH_2PO_4, 10 mM Li_2HPO_4, and 1 mM NaCl, pH = 7.2) was added into the electrode body, and a Ag/AgCl wire was inserted as inner reference electrode. Prior to measurements, all electrodes were conditioned in a 10 mM LiH_2PO_4 solution. The conditioning process was monitored by measuring the EMF (electromotive force). In this first contact with an electrolyte solution, it typically took several hours until the membranes had equilibrated with the aqueous solutions and a completely stable potential was obtained.

For the ionophore-free ion exchanger electrodes, small disks of membranes were cut from parent membranes and mounted into Phillips-type electrode bodies (Glasbläserei Möller, Zürich, Switzerland). The inner filling solution was a 1 mM KCl solution, and the resulting electrodes were conditioned in 100 mM KCl solution for 24 h prior to measurements.

EMF and Resistance Measurements. Potentials were monitored with an EMF 16 potentiometer (Lawson Labs Inc., Malvern, PA) controlled with EMF Suite 1.02 software (Fluorous Innovations, Arden Hills, MN) at room temperature (25 °C) and with stirred solutions. The external reference electrode (DX200, Mettler Toledo, Greifensee, Switzerland) consisted of a double-junction Ag/AgCl electrode with a 1.0 M LiOAc bridge electrolyte and 3.0 M KCl as reference electrolyte. An InLab 201 pH half-cell glass electrode (Mettler Toledo, Columbus, OH) was used to monitor the pH value of the sample solutions for all measurements of response curves and selectivities. The glass pH electrode was calibrated by a five-point calibration with reference buffer solutions of pH 4.00, 7.00, 10.01, 12.00, and 13.00. The responses to H^+ were measured by adding HCl to 100 mL of a 0.05 M Tris buffer of pH = 9.0 (prepared from 50 mL of 0.1 M Tris and 5.7 mL of 0.1 M HCl). Selectivity coefficients were determined with the fixed interference method.[26] For this purpose, the starting solutions all contained 15 mM HCl, 10 mM Tris, and 100 mM of the chloride salt of the interfering ions of interest. In the case of Na^+ and K^+ selectivity measurements, aliquots of 100 mM NaOH or KOH solutions were added into the starting solution to change the pH, respectively. For Ca^{2+} selectivity measurements, due to the low solubility of $Ca(OH)_2$, 1 M LiOH was added rather than $Ca(OH)_2$ to increase the pH until precipitation was observed. Selectivity coefficients reported are averages for four to six electrodes. For ion exchange electrodes, response curves to K^+ were obtained by repeated dilution of the sample with pure water, starting with a 100 mM KCl solution. Activity coefficients were calculated with a two-parameter Debye−Hückel approximation.[27]

DC resistances of sensing membranes were determined using the method of potential reduction by a known shunt,[28,29] using the

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same type of 1.0 GΩ resistors (±0.01 GΩ, 2.5 W, Digi-Key, Thief River Falls, MN) as in our previous work.[7]

Characterization of Teflon AF2400 by IR Spectroscopy. To study the properties of Teflon AF2400, 250 mg (0.8 μmol) of this polymer was dissolved in 15 mL of perfluorohexane, and 40 μL (30 mg, 0.5 mmol) of 1-propylamine was added. The solution was refluxed overnight at 50 °C in an Ar atmosphere and then cooled to room temperature. After removal of the solvent with a rotary evaporator and drying of the resulting residue for 24 h under vacuum to remove excess 1-propylamine, the reaction product was dissolved in 3 mL of perfluorohexane. The solution was poured into a casting mold made of a glass ring (2.5 cm in diameter and 1.3 cm in height) that was held tightly to a glass plate with rubber bands. A sheet of Teflon was placed between the glass ring and the plate to facilitate removal of the dried polymer films from the mold after 24 h at ambient pressure to permit evaporation of the perfluorohexane solvent. In control experiments, thin films of untreated Teflon AF2400 were prepared in the same fashion. The thickness of the resulting films was 60 μm. IR spectra of these films were taken with a MIDAC M series FTIR spectrometer (Costa Mesa, CA).

Results and Discussion

Preliminary experiments were performed using self-supporting ion-exchanger membranes with blends of the perfluoropolymer Teflon AF2400 and linear perfluorooligoether (70%/30%), doped with the fluorophilic borate salt **3** to provide for ionic sites. Unlike in our previous experiments with perfluorocarbons of low molecular weight as fluorous matrixes, no porous support to hold the sensing phase was used.[7,8,18,19] However, the poor solubility of **3** in the linear perfluorooligoether (0.19 mM, as determined by ^{1}H NMR spectroscopy) resulted in an unacceptably high electrical resistance and a poor reproducibility of the potentiometric responses. On the basis of the hypothesis that a salt consisting of tetrakis[3,5-bis(perfluorohexyl)phenyl]borate as anion and an ionophore complex as cation would be more soluble in the fluorous phase than the sodium salt **3**, it was decided to perform all subsequent experiments with ionophore-doped membranes. Also, to be able to study the effect of the polymer on membrane resistances and selectivities, membranes with varying Teflon AF2400 contents were subsequently prepared by infusion of the ionophore- and site-doped perfluoropolymer/plasticizer blends into porous Fluoropore membrane filters made of poly(tetrafluoroethylene). Because these porous filters do not swell in any organic or fluorous solvent, their role for these sensing membranes is merely to provide an inert mechanical support, holding in its fully interconnected pores the ionophore-doped fluorous sensing phase. It is important to note, however, that these porous membrane supports are not necessary for the preparation of self-supporting membranes with high Teflon AF2400 contents.

Four fluorophilic H^+ ionophores were available to us from previous work.[19] The most selective one had been found to be so selective that K^+, Na^+, and Ca^{2+} interferences could not be determined quantitatively even at the highest pH and metal ions concentrations. For example, the selectivity for H^+ over Na^+ was found to be larger than $1{:}10^{13.5}$ ($\log K^{\text{pot}}_{\text{H,Na}} < -13.5$). To permit a quantitative discussion of the sensor performance of fluorous polymeric membranes, it was, therefore, decided to use not the most selective of the available ionophores but rather the somewhat less selective ionophore tris[(perfluorooctyl)propyl]amine, **4**, which has three CH_2 spacers between the H^+ binding nitrogen atom and the fluorinated carbon atoms. Fluorous pH sensors based on this ionophore, ionic sites (**3**), and perfluoroperhydrophenanthrene as the fluorous membrane matrix were previously found to exhibit logarithmic selectivity coefficients, $\log K^{\text{pot}}_{\text{H,J}}$, of −7.9, −9.3, and <−10.8 for K^+, Na^+, and Ca^{2+}, respectively.[19]

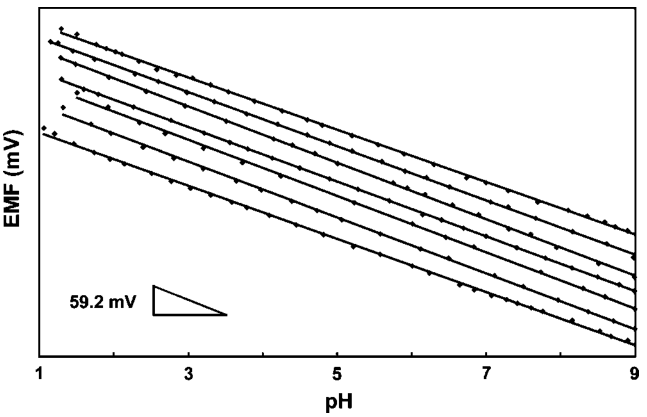

Figure 1. EMF responses of fluorous membrane ISEs to H^+ in Tris-HCl buffer. Each sensing membrane was composed of 2 mM fluorophilic ionophore, 0.5 mM fluorophilic ionic sites, and Teflon AF2400 contents between 0% and 25% in linear perfluorooligoether **2** (from bottom to top). For clarity, response curves are shifted vertically relative to one another.

EMF Responses. The H^+ responses of electrodes with 2 mM ionophore (**4**), 0.5 mM ionic sites (**3**), the linear perfluorooligoether (**2**), and different amounts of Teflon AF2400 were tested by addition of HCl to Tris-HCl buffer solution (see Figure 1). All electrodes showed Nernstian responses to H^+ in the pH range from 2 to 9. The use of ionophore enhanced the solubility of the ionic sites, and no precipitation of ionophore or ionic sites within the sensing membranes was observed.

Electrical Membrane Resistances. Blends of linear perfluorooligoether and Teflon AF2400 in all of the ratios tested for ISE membranes have glass transition temperatures, T_g, much lower than room temperature, suggesting that the ion mobilities of the fluorophilic anions and ionophore complexes in the ISE membranes are sufficiently high to give EMF responses with a low noise level (see T_g values in Table S1 of the Supporting Information). Indeed, the electrical resistances of the sensing membranes with relatively low polymer contents were found to be similar to the resistance of polymer-free membranes (Figure 2). However, the resistance of the ISE membranes increased by nearly 2 orders of magnitude with a polymer concentration of 25%. This is a much bigger increase than would be expected on the basis of the Mackie−Meares obstruction model for solute diffusion in heterogeneous media, which upon combination with the Nernst−Einstein equation ($\sigma = cz^2F^2D/RT$) gives[30,31]

$$\frac{\sigma_m}{\sigma_0} = \left(\frac{1-\varphi}{1+\varphi}\right)^2 \tag{1}$$

where σ_0 and σ_m are the ionic conductivities of solutes in a polymer-free solution and in a polymeric membrane, respectively, and φ is the volume fraction of the polymer network. A prediction of the electrical membrane resistance based on eq 1 is shown in Figure 2 (dashed curve). Clearly, the Mackie−Meares obstruction model severely underestimates the resistances of the sensing membranes with higher polymer concentrations. Because obstruction theory assumes that the polymer network only

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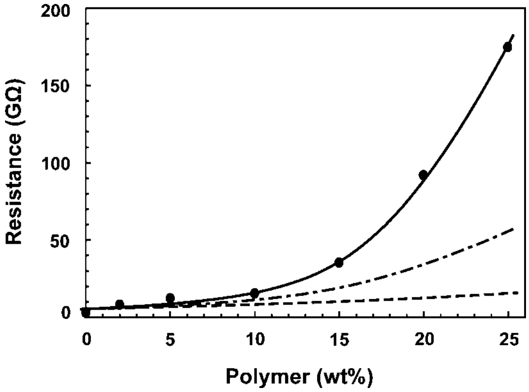

Figure 2. Effect of the polymer content on the experimentally observed electrical resistance of the sensing membranes (●), along with a prediction based on the Mackie−Meares obstruction model (- - -), a modified model taking into account the additional interaction due to the functional group X in the polymer (− - −), and a model considering both the functional group X and the triple ion formation (−; $K_{L_2H} = 10^{5.5}$ M^{-1}, $K_{LX} = 10^{4.4}$ M^{-1}, $K_{ip,L_2HR} = 10^{12}$ M^{-1}, $K_{t,RL_2HR} = 10^{5.5}$ M^{-1}). Membrane compositions are the same as for Figure 1.

blocks the pathway of solutes but does not affect their mobility, the much larger than expected resistances suggest that there is some interaction between the polymer and other membrane components. Binding of H^+, H^+−ionophore complexes, or the fluorophilic anions of **3** to the dioxole units of the polymer backbone cannot explain this observation because previous work has confirmed that perfluorooligoethers are only extremely weakly coordinating.[8] Moreover, simulations show that the membrane resistance would increase much more gradually with the increasing polymer concentration (not shown). Instead, the experimentally observed resistance is only moderately affected by the presence of the polymer at 5%, 10%, and 15% Teflon AF2400, but then rises quite rapidly for polymer contents of 20% and 25%. Also, the resistance of a membrane containing 4.0 mM ionophore (**4**), 0.5 mM ionic sites (**3**), linear perfluorooligoether (**2**), and 25% Teflon AF2400 was nearly 10 times lower (18.3 GΩ) than the resistance of a membrane with 2.0 mM ionophore and an otherwise identical composition (175 GΩ). Both observations can be explained by the presence of functional groups on Teflon AF2400 that interact with the free ionophore. This can be shown by a modification of the Mackie−Meares model, as described quantitatively in the following.

As discussed in previous work with fluorous phases, ion pair formation constants in these low polarity media are so high that the concentration of free ions is extremely low.[7] The poor solvation in fluorous solvents favors the formation of a hydrogen-bonded heterodimer, L_2H^+, between the free uncomplexed ionophore, L, and the protonated ionophore LH^+.

$$\mathrm{L(mem)} + \mathrm{H^+(mem)} \rightleftharpoons \mathrm{LH^+(mem)} \qquad (2)$$

$$\mathrm{L(mem)} + \mathrm{LH^+(mem)} \rightleftharpoons \mathrm{L_2H^+(mem)} \qquad (3)$$

As a result, the majority of ions in our fluorous ionophore-doped membranes are expected to be present in the form of the ion pairs $L_2H^+{\cdot}R^-$, where R^- represents the fluorophilic anions of **3**. In the absence of polymer, the 1:4 ratio of ionic sites to ionophore ensures that there is an excess of uncomplexed ionophore, L, and that the concentration of LH^+ that is not part of a L_2H^+ heterodimer is low. The functional group, X, of Teflon AF2400 disturbs this equilibrium by binding to the free ionophore, L:

$$\mathrm{L(mem)} + \mathrm{X(mem)} \rightleftharpoons \mathrm{LX(mem)} \qquad (4)$$

At high enough concentrations of polymer, this results in a decrease in the concentration of $L_2H^+{\cdot}R^-$ ion pairs, and an increase in the concentration of $LH^+{\cdot}R^-$ ion pairs:

$$\mathrm{L_2HR(mem)} + \mathrm{X(mem)} \rightleftharpoons \mathrm{LHR(mem)} + \mathrm{LX(mem)} \qquad (5)$$

This is accompanied by a major change in membrane resistance. To quantitatively describe this effect, the formation of triple ions cannot be ignored, as shown similarly for a variety of ionic solutions in solvents of low polarity including fluorous membranes.[32] The only triple ions considered here are those that are formed by two fluorophilic anions and one L_2H^+ cation:

$$\mathrm{L_2H^+(mem)} + \mathrm{R^-(mem)} \rightleftharpoons \mathrm{L_2H{\cdot}R(mem)} \qquad (6)$$

$$\mathrm{R^-(mem)} + \mathrm{L_2H{\cdot}R(mem)} \rightleftharpoons \mathrm{R{\cdot}L_2H{\cdot}R^-(mem)} \qquad (7)$$

In an attempt to explain the experimental observations with a minimum of parameters, the formation of $L_2H^+{\cdot}R^-{\cdot}L_2H^+$ is ignored here because the heterodimer L_2H^+ is much larger than the borate derivative R^-, suggesting that the stability of $L_2H^+{\cdot}R^-{\cdot}L_2H^+$ is much smaller.

After numerical calculation of the concentration of all species involved in the above equilibria, taking into account all equilibrium constants, mass balances for L, R^-, and X, and electroneutrality, the specific membrane conductivity, κ (which is inversely related to the resistance), can then be obtained as

$$\kappa = (\lambda_{H^+}[H^+]_{mem} + \lambda_{LH^+}[LH^+]_{mem} + \lambda_{L_2H^+}[L_2H^+]_{mem} + \lambda_{R^-}[R^-]_{mem} + \lambda_{RL_2HR^-}[RL_2HR^-])_{mem}\left(\frac{1-\varphi}{1+\varphi}\right)^2 \qquad (8)$$

where the λ_i are the limiting molar conductivities of each ion, and the rightmost expression in parentheses represents a correction term according to the Mackie−Meares obstruction theory (for a more detailed description, see the Supporting Information).

Two constants describing binding of H^+ to the ionophore ($K_{LH} = 10^{9.8}$ M^{-1}) and the ion-pair formation of protonated ionophore and ionic sites ($K_{ip,LHR} = 10^{15.2}$ M^{-1}) were experimentally determined previously for the same ionophore in the very similar solvent perfluoroperhydrophenanthrene[19] and were used here to explain the experimental resistance data with eq 8. (Note that perfluoroperhydrophenanthrene has a dielectric constant ($\varepsilon = 2.03$) that is only 0.13 higher than that of Teflon AF2400 and 0.04 lower than that of the linear perfluorooligoether.)[33−35] The remaining parameters were obtained from a simultaneous fit of the experimental dependence of the resistances and the Na^+, K^+, and Ca^{2+} selectivities ($\log K^{pot}_{H,J}$) of these membranes (see below and the Supporting Information) using a multidimensional downhill simplex algorithm[36] written for this purpose in Mathematica 6.0.

As Figure 2 shows, eq 8 provides an excellent fit to the experimental data. The fitted triple ion formation constant ($K_{t,RL_2HR} = 10^{5.5\pm0.4}$ M^{-1}) is relatively close to the experimental value observed in perfluoroperhydrophenanthrene membranes ($10^{4.5}$ M^{-1}).[19] Other parameters obtained from the simplex fit include the constants describing the stabilities of the complexes

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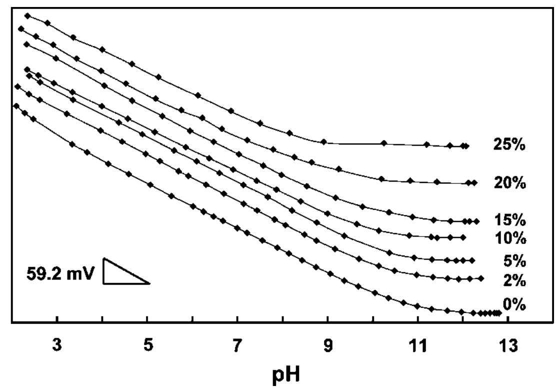

Figure 3. Selectivity measurements: EMF responses of fluorous pH ISEs in 10 mM Tris buffer with a constant background of 0.1 M Na^+. Membrane compositions are the same as for Figure 1. For clarity, response curves are shifted vertically relative to one another.

of ionophore and protonated ionophore ($K_{L_2H} = 10^{5.5}$ M^{-1}), the functional group X of Teflon AF2400 and unprotonated ionophore ($K_{LX} = 10^{4.4}$ M^{-1}), the ion-pair $L_2H^+ \cdot R^-$ ($K_{ip,L_2HR} = 10^{12}$ M^{-1}), and the concentration of the functional groups X, which is found to have the surprisingly low value of one functional group per 854 monomer units of Teflon AF2400. A 95% confidence interval for the latter was estimated by bootstrapping to be approximately 9% (see the Supporting Information).

Importantly, the fitted parameters all have distinct effects on the resistance and selectivities and are indeed necessary to obtain good fits to the experimental data. This is illustrated by the dependence of the membrane resistance on different parameters, as predicted by eq 8. For example, if the interactions between the ionophore and the functional groups X were negligibly weak ($K_{LX} = 10^{-3}$ M^{-1}), the resistances as predicted by eq 8 would be identical to those predicted by the poorly fitting unmodified Mackie−Meares model (Figure 2, dashed line). Also, a very poor fit is obtained when the formation of triple ions is ignored (Figure 2, dash-dotted line). Moreover, if binding of ionophore to protonated ionophore was negligibly weak ($K_{L_2H} = 10^{-3}$ M^{-1}), a 2.78-fold increase in resistance for the change from 0 to 25% polymer concentration would be expected (not shown), which is the same relative increase in resistance as is predicted by the Mackie−Meares obstruction model. Indeed, the resistance prediction for $K_{L_2H} = 10^{-3}$ M^{-1} overlaps perfectly with the poor Mackie−Meares fit if the former assumes values of the limiting molar conductivities that are 66 times larger than those for the best fit shown in Figure 2.

Potentiometric Selectivities. The experimentally observed selectivity coefficients log $K^{pot}_{H,J}$ of sensing membranes based on linear perfluorooligoether but no Teflon AF2400 were determined to be −8.75, −9.76, and −9.44 for K^+, Na^+, and Ca^{2+}, respectively. These selectivities are similar to those of fluorous liquid membranes based on perfluoroperhydrophenanthrene doped with the same ionophore (−7.9, −9.3, and <−10.8, respectively).[19] However, as with the resistances, the potentiometric selectivities are affected by the Teflon AF2400 content of the membrane matrixes. Responses of these electrodes to pH in a fixed background of the interfering ion Na^+ show the Na^+ interference at high pH as a leveling off of the EMF response (see Figure 3). Indeed, this figure illustrates that, because of the Na^+ interference caused by the Teflon AF2400, the detection limit for H^+ becomes higher as the Teflon AF2400 content increases. This is also reflected in the selectivity coefficients log $K^{pot}_{H,J}$ (see Table 1).

Table 1. Proton Selectivities (log $K^{pot}_{H,J}$) of Fluorous Ionophore-Doped pH Membranes Based on the Linear Perfluorooligoether **2** and Different Amounts of Teflon AF2400[a]

	proton selectivity (log $K^{pot}_{H,J}$)		
Teflon AF2400 (wt %)	Na^+	K^+	Ca^{2+}
0	−9.76 ± 0.09	−8.75 ± 0.04	−9.44 ± 0.11
2	−9.49 ± 0.04	−8.49 ± 0.02	−8.98 ± 0.16
5	−9.39 ± 0.02	−8.31 ± 0.01	−8.81 ± 0.12
10	−9.05 ± 0.11	−7.89 ± 0.14	−7.68 ± 0.27
15	−9.01 ± 0.04	−7.80 ± 0.06	−7.59 ± 0.18
20	−8.27 ± 0.19	−7.36 ± 0.10	−7.16 ± 0.11
25	−7.45 ± 0.18	−6.79 ± 0.10	−6.79 ± 0.17

[a] [ionophore] = 2 mM, [ionic sites] = 0.5 mM.

At first sight, the effect of Teflon AF2400 on the selectivity coefficients log $K^{pot}_{H,J}$ seems more complex than it is in the case for the membrane resistance. Even a few percent of Teflon AF2400 causes a small reduction of the selectivities for H^+ over all three metal cations, but up to 15% Teflon AF2400 the effect of additional polymer is small. However, as in the case of the resistance, an additional reason for selectivity loss seems to arise for polymer concentrations higher than 15%, where a more pronounced selectivity reduction occurs.

It is shown in the following that the small loss of selectivity at low polymer concentrations can be explained by binding of the metal cations to the dioxole units of the polymer, and the larger selectivity loss at higher polymer concentrations is the result of the equilibria already considered above for the discussion of the resistance data. As described previously, the phase boundary model of ionophore-based ISEs[37,38] shows that the selectivity coefficient, $K^{pot}_{H,J}$, can be obtained from:

$$K^{pot}_{H,J} = \frac{[H^+]_{mem}}{(K_{ex,HJ}[J^{z+}]_{mem})^{1/z}} \tag{9}$$

where z is the charge of J, $[J^{z+}]_{mem}$ is the concentration of uncomplexed interfering ion in the bulk of the sensing membrane when the membrane is exposed to an aqueous solution with a concentration of J^{z+} to which the electrode exhibits a Nernstian response, and $[H^+]_{mem}$ is the membrane concentration of H^+ when the electrode is exposed to an aqueous solution of a pH for which the electrode exhibits a Nernstian response. $K_{ex,HJ}$ is the equilibrium constant for the ion-exchange of H^+ and J^{z+} between the sample and membrane phases in the absence of ionophore:

$$H^+(aq) + \frac{1}{z}J^{z+}(mem) \rightleftharpoons H^+(mem) + \frac{1}{z}J^{z+}(aq) \tag{10}$$

$[H^+]_{mem}$ is obtained by solving the set of equations describing the equilibria already outlined in the discussion of the resistance data, the mass balances for L, R^-, X, and electroneutrality. In addition, for each ion J^{z+}, the following equilibria for binding of J^{z+} to the dioxole units of Teflon AF2400 and to the functional group X are taken into account (for a more detailed discussion, see the Supporting Information):

$$P(mem) + J^{z+}(mem) \rightleftharpoons PJ^{z+}(mem) \tag{11}$$

$$X(mem) + J^{z+}(mem) \rightleftharpoons XJ^{z+}(mem) \tag{12}$$

Equations to calculate log $K^{pot}_{H,J}$ for Na^+, K^+, and Ca^{2+} as a function of the parameters $K_{ex,HJ}$, K_{PJ}, and K_{XJ} were included in the already mentioned downhill simplex algorithm that was used

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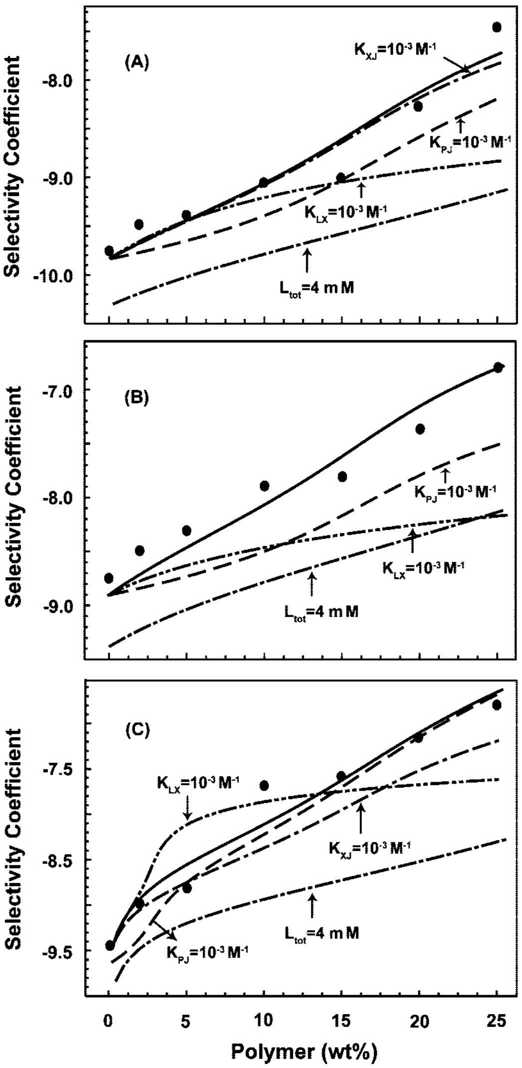

Figure 4. Experimental selectivity coefficients, log $K^{\mathrm{pot}}_{\mathrm{H,J}}$, of fluorous sensing membranes with different Teflon AF2400 contents (●): Selectivities for H^+ over (A) Na^+, (B) K^+, and (C) Ca^{2+}. Best fits based on the same parameters as for the best fit in Figure 2 and $K_{\mathrm{PNa}} = 1.9$ M^{-1}, $K_{\mathrm{PK}} = 2.6$ M^{-1}, $K_{\mathrm{PCa}} = 82$ M^{-1}, $K_{\mathrm{XNa}} = 10^{3.5}$ M^{-1}, $K_{\mathrm{XK}} = 10^{1.8}$ M^{-1}, $K_{\mathrm{XCa}} = 10^{6.8}$ M^{-1}, $K_{\mathrm{ex,HNa}} = 10^{-3.5}$, $K_{\mathrm{ex,HK}} = 10^{-4.4}$, and $K_{\mathrm{ex,HCa}} = 10^{-10.4}$ (—). Also shown are selectivities as predicted for $K_{\mathrm{PJ}} = 10^{-3}$ M^{-1} (− − −), $K_{\mathrm{XJ}} = 10^{-3}$ M^{-1} (− − •; in A this fit partly overlaps with the best fit, and in B it completely overlaps with the best fit), $K_{\mathrm{LX}} = 10^{-3}$ M^{-1} (− • •), and $[L]_{\mathrm{tot}} = 4$ mM (− • − •). In all four cases, parameters not mentioned are as for the best fit. Membrane compositions are the same as for Figure 1.

to fit the experimental resistances and the Na^+, K^+, and Ca^{2+} selectivities shown in Figures 2 and 4A−C. Figure 4 shows that, within experimental error, the fit provides for a very good explanation of the experimentally observed selectivities over all three metal cations. The fact that this fit required, in addition to the parameters already used for the discussion of the resistance data, only three parameters for each interfering ion, and this despite the complicated, experimentally observed dependence log $K^{\mathrm{pot}}_{\mathrm{H,Na}}$, log $K^{\mathrm{pot}}_{\mathrm{H,K}}$, and log $K^{\mathrm{pot}}_{\mathrm{H,Ca}}$ on the polymer concentration, is noteworthy. It is an indication that the membrane model used here gives a good description of the equilibria occurring in these ionophore-doped membranes.

As for the resistance data, the possibility to predict log $K^{\mathrm{pot}}_{\mathrm{H,J}}$ functions for different sets of parameters enables a more detailed interpretation of the selectivity changes. Such calculations show, for example, that if the constants K_{PJ} for binding of Na^+ to the dioxole units of Teflon AF2400 were negligibly small (10^{-3} M^{-1}), the effect of the polymer concentration on the selectivities over Na^+ would be much smaller in the concentration range between 2% and 10% polymer (Figure 4A, dashed curve). This confirms that binding of Na^+ to the polymer backbone of Teflon AF2400 cannot be ignored. Indeed, the binding constant, K_{PNa}, which was determined with the simplex fit to be 1.9 M^{-1} (log $K_{\mathrm{PNa}} = 0.16 \pm 0.71$), is within error identical to the one reported for interactions between a perfluorinated tetraether and Na^+ in perfluoroperhydrophenanthrene (2.3 M^{-1}).[8] A similar binding constant of K^+ to the polymer backbone of Teflon AF2400 was obtained ($K_{\mathrm{PK}} = 2.6$ M^{-1}, log $K_{\mathrm{PK}} = 0.35 \pm 0.59$) from the simplex fit, and as with Na^+ the dashed curve in Figure 4B confirms that, although weak, this interaction with the polymer does have a small but distinct effect on selectivities.

In the case of Ca^{2+}, cation binding to the dioxole units has a surprisingly small effect on selectivities because the Ca^{2+}−dioxole interaction competes with a much stronger interaction of Ca^{2+} with the functional groups X. On the one hand, the calculated selectivity over Ca^{2+} when a very weak interaction of Ca^{2+} with the dioxole units is assumed ($K_{\mathrm{PCa}} = 10^{-3}$ M^{-1}; Figure 4C, dashed curve) differs very much from that of the best-fit prediction with $K_{\mathrm{PCa}} = 82$ M^{-1} only at low polymer concentrations (Figure 4C, solid line). On the other hand, at higher polymer concentrations, the selectivity over Ca^{2+} predicted for a very weak interaction with the functional group X ($K_{\mathrm{XCa}} = 10^{-3}$ M^{-1}, dash-dash-dotted curve) gives a higher discrimination of Ca^{2+} than the experimental data and the best-fit prediction with $K_{\mathrm{XCa}} = 10^{6.8}$ M^{-1}. This confirms that the interaction of the functional group X and Ca^{2+} is significant and shows that the reason for the absence of a bigger effect of K_{PCa} on the discrimination of Ca^{2+} can be found in the strong binding of X to Ca^{2+}, preventing the latter from interacting with the dioxole units. In contrast, the very small hypothetical K_{XNa} and K_{XK} values of 10^{-3} M^{-1} (dash-dash-dotted curves in Figure 4A and B, respectively) do not give selectivities appreciably different from those obtained with the K_{XNa} and K_{XK} values of $10^{3.5}$ and $10^{1.8}$ M^{-1}, respectively, as they are provided by the simplex fit. This can be explained by a combination of the very low concentration of the functional group X and the weakness of the interaction.

As seen similarly for the resistance data, the interaction of the functional group X with the ionophore has a particularly pronounced effect on the selectivities at the highest polymer concentrations. Figure 4 shows that, for all three metal cations, all of the selectivities calculated for $[L]_{\mathrm{tot}} = 2$ mM, $K_{\mathrm{LX}} = 10^{4.4}$ M^{-1}, and different sets of other parameters (including the best fit one) exhibit two inflection points at high polymer concentrations. A region of increased slope due to incipient depletion of X starts at about 10% Teflon AF2400, which is followed at about 20% by a return to a somewhat smaller slope in the presence of an excess of X. Consistent with this interpretation, these inflection points are absent, and the loss of selectivity with increasing polymer concentration is less pronounced, if $K_{\mathrm{LX}} = 10^{-3}$ M^{-1} is assumed (dash-dot-dotted lines). Also, inflection points for the selectivities calculated with $[L]_{\mathrm{tot}} = 4$ mM are shifted to higher polymer concentrations and cannot be discerned in the 0−25% polymer concentration range shown in Figure 4. This again confirms the importance of considering this functional group X.

Yet another confirmation for this membrane model, and also an indication of how to minimize the effect of the functional group X, comes from a very simple experiment in which the selectivities were determined for membranes with 25% of Teflon

AF2400, linear perfluorooligoether **2** as plasticizer, and the same amount of ionic sites (0.5 mM) but twice as much ionophore **4** (4 mM) than for all other results shown in Figure 4. The observed log $K^{\text{pot}}_{\text{H,J}}$ values were −8.97 ± 0.11, −8.39 ± 0.22, and −9.09 ± 0.28 for Na^+, K^+, and Ca^{2+}, respectively. These results differ by nearly an order of magnitude from those for the membranes with 2 mM ionophore **4**, but they match well with the predictions from theory (dash-dotted curves in Figure 4).

Identity of the Functional Groups X. The simplex fit of the resistance and selectivity data showed that one functional group X occurs per 854 monomer units of the polymer Teflon AF2400. Interestingly, an average of 620 monomer units per polymer chain is calculated from the dioxole content of 87% and the molecular weight of 3×10^5.[34] This suggests that both the resistance and the selectivity measurements are equivalent to a titration of terminal groups of Teflon AF2400, apparently introduced by radical polymerization of Teflon AF2400. Initiators for this polymerization, as reported in the patent literature, are 4,4′-bis(*tert*-butylcyclohexyl)peroxydicarbonate and (ammonium or potassium) persulfate,[39] which can form carboxyl radicals and sulfate anion radicals, respectively. Interestingly, the absence of sulfur in poly(tetrafluoroethylene) polymerized with persulfate as initiating reagent has been interpreted as resulting either from the quick hydrolysis of sulfate esters or from the formation of hydroxyl radicals as the true polymerization initiators. Hydrolysis could also occur in the case of esters formed from peroxydicarbonate initiators.[40] In all cases, the resulting difluorocarbinols are not very stable but decompose to form carboxylic acid fluorides, which can further hydrolyze to give carboxylic acid groups.[41] Indeed, it appears very likely that the functional groups X observed in this work are carboxyl groups, as this explains both the binding of the functional group X to the amino group of the unprotonated ionophore as well as the binding to Ca^{2+}.

The hypothesis that the X groups are carboxyl groups is supported by potentiometric experiments with sensing membranes containing fluorophilic cationic sites provided by tris[(perfluorooctyl)propyl]methylammonium methyl sulfate (**5**, 1.0 mM),[8,25] linear perfluorooligoether (**2**), and 25% Teflon AF2400. If there were no ionizable groups on Teflon AF2400, these membranes would respond to anions, as previously demonstrated for fluorous membranes made of the same cationic site and perfluoroperhydrophenanthrene as matrix.[18] Instead, the membranes with Teflon AF2400 give a Nernstian pH response in the range of pH 1.6−4.2 (for a graph, see Figure S1 in the Supporting Information). This is the well-known behavior of potentiometric membranes that contain cationic sites and functional groups acting as negatively charged ionophores[37,42,43] for H^+, as is expected for carboxylate groups. To confirm that carboxyl groups can indeed be deprotonated in a fluorous phase and act as electrically charged ionophores, experiments were also performed with the same cationic sites (**5**, 2.0 mM) and the perfluorooligoether Krytox157FS-H, which has terminal carboxyl groups.[44] Indeed, the membranes exhibited quite similar responses, with Nernstian responses to H^+ at low pH (1.3−2.6; see Figure S1 in the Supporting Information). These experiments give strong support to the interpretation that Teflon AF2400 has functional groups that can be deprotonated, and it appears likely that these are carboxyl groups.

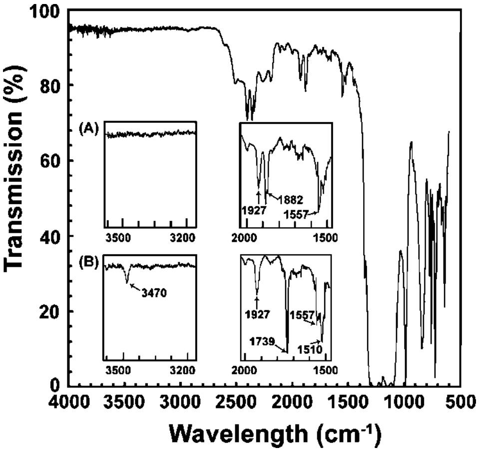

Figure 5. IR spectrum of a thin film of unreacted Teflon AF2400. Insets show magnified regions of (A) unreacted Teflon AF2400 and (B) Teflon AF2400 reacted with 1-propylamine. After the reaction with 1-propylamine, the C(=O)F at 1882 cm^{-1} disappeared, and the amide peaks at 1739 and 1510 cm^{-1} as well as an NH stretch band at 3470 cm^{-1} appeared.

This conclusion is also confirmed by the IR spectra of Teflon AF2400 before and after exposure to 1-propylamine. The IR spectra observed of a neat film of untreated Teflon AF2400 (see Figure 5) show a weak but distinct peak at 1882 cm^{-1}. At first sight, this peak is easily mistaken for an overtone or combination band, similar to the one at 1927 cm^{-1}. However, the 1882 cm^{-1} peak is exactly where carboxylic acid fluorides are expected.[45,46] Moreover, when Teflon AF2400 is refluxed overnight with 1-propylamine, the C(=O)F peak (1882 cm^{-1}) disappears, and an amide I band at 1739 cm^{-1}, an amide II at 1510 cm^{-1}, and a NH stretch at 3470 cm^{-1} appear at positions expected for an amide derivative of a carboxylic acid with at least one fluoro substituent in α position.[47] Clearly, the carboxylic acid fluoride groups of Teflon AF2400 react with the amine to give amide groups. Similarly, the C(=O)F groups of freshly prepared ISE membranes containing Teflon AF2400 can hydrolyze when they are exposed to aqueous solution, explaining the observation of carboxylic acid groups in the potentiometric experiments.

Long-Term Stability of Electrodes. The long-term stabilities of the fluorous membrane electrodes with different Teflon AF2400 contents were determined by measuring H^+ responses and selectivities every 3 days over 4 weeks. Between each measurement, the electrodes were stored in 10 mM LiH_2PO_4 solution. The results show that even after 4 weeks, the electrodes still exhibit a Nernstian response to H^+. The standard deviations of the response slopes are lower than 0.54 mV/decade for all electrodes (see Table S3 in the Supporting Information). Figure 6 shows that there are hardly any changes in selectivities over

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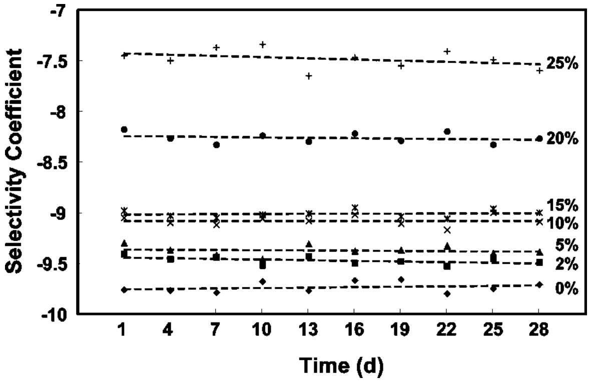

Figure 6. Long-term stability of fluorous membranes with polymer contents between 0% and 25% (wt/wt): Selectivity coefficients log $K^{pot}_{H,Na}$ over a period of 4 weeks of use.

time. These results confirm that these electrodes have a very favorable long-term stability.

Conclusions

This work introduced the first ionophore-doped ISEs with fluorous polymeric matrixes. They exhibited the response slopes predicted by theory, the high selectivity of Na^+, K^+, and Ca^{2+} expected for this ionophore, and a favorable long-term stability enhanced by the polymer matrix. Moreover, membranes with 30% Teflon AF2400 do not require a porous support to maintain their shape under typical working conditions. The analysis of the effect of the polymer on the selectivities shows that metal cation interactions with the dioxole units of the perfluoropolymer Teflon AF2400 affect selectivities only very weakly. However, a functional group of Teflon AF2400 has a larger effect on the selectivities of sensor membranes if the polymer concentration is higher, which can be explained by rather strong interactions of these functional groups with both the ionophore and the Ca^{2+}. One of these functional groups was found to occur once per 854 monomer units of the polymer, with experimental evidence indicating that these are carboxyl groups. This effect can be minimized by use of higher ionophore concentrations. Alternatively, these carboxyl groups could be eliminated reductively, or by reaction of the initial acid fluoride groups of Teflon AF with an amine. Moreover, the existence of $C(=O)F$ groups opens the possibility to modify Teflon AF2400 for different goals, such as the covalent attachment of ionophores or ionic sites to improve detection limits and prevent the loss of these species by partitioning into samples.

The use of these blends of Teflon AF2400 and linear perfluorooligoethers as matrixes for ISEs based on other ionophores is straightforward and makes ISEs with fluorous polymeric membranes for a wide variety of different ions possible. The optical transparency of these matrixes down to well below 200 nm would be also a distinct advantage for the preparation of ionophore-based optodes, which are based on a well-known response model closely related to that of ISEs.[3] Moreover, the minimal absorption of these fluorous matrixes in the infrared range above 1600 cm^{-1} opens a way to analogous infrared sensors. Applications of these highly inert fluorous polymeric membranes are, however, not limited to chemical sensing. Receptor-assisted extraction systems with Krytox, which is a carboxylic acid-terminated perfluoropolypropylene oxide, have already been reported[22,48] and could be prepared with the polymer blends described here. Also, receptor-based phase transfer into fluorous phases has been used for synthetic purposes in the context of biphasic and triphasic catalysis,[11,12] for which the availability of thin fluorous polymeric membranes permitting high transport rates should be a distinct advantage.[48] For these and many other applications, the characterization of the inertness of Teflon AF as described in this work will be very valuable.

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Supporting Information Available: Resistances of membranes with different polymer contents, and response slopes of electrodes in long-term stability measurement. Extensive description of the calculation of resistances and selectivities for specific sets of parameters, and the simplex algorithm used to fit the experimental data. Table of all fitted parameters along with error estimates. Potentiometric responses of ISE membranes with cationic sites and Teflon AF2400 or Krytox 157FS-H. This material is available free of charge via the Internet at http://pubs.acs.org.

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